

# Transition-metal silicides lattice-matched to silicon

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We have used a systematic search to determine all the possible transition-metal silicides that are geometrically lattice-matched to either the (100), (110), or the (111) face of silicon. A short table with the best possible matches is presented here, and a more comprehensive table including slightly worse matches is deposited with the editor.

Recently, there has been a considerable interest in thin films of transition-metal silicides grown epitaxially on silicon.<sup>1-5</sup> The traditional application of transition-metal silicides is as contacts and interconnects; this application uses their metallic character and their ability to be oxidized or to withstand high temperatures. Transition-metal silicides also have possible applications in novel devices.<sup>6-9</sup>

The problem of epitaxial growth is complicated. One of the factors that can be of relevance to epitaxial growth is the lattice mismatch. In a previous paper<sup>10</sup> we have described a general method that enables one to find systematically all the possible matching faces of any pair of crystalline materials. In this paper we apply this method to the interfaces of transition-metal silicides on silicon, and thereby obtain the most comprehensive tabulation of such lattice matches for this system. Partial lists were published before.<sup>2,11</sup> The silicides that were considered are those of the three transition periods in the periodic table (columns IIIA through IB) including lanthanum, but not the other lanthanides.

The precise definition of lattice match, as well as a systematic procedure to find them, was given in a previous publication<sup>10</sup>; we shall repeat here only the essential definitions and concepts. By "lattice match" we mean a periodic translational symmetry of the interface that is compatible with the crystal structures on both sides of that interface. To understand this definition, refer to Fig. 1, in which we show a hypothetical lattice match between  $V_3Si(111)$  and  $Si(111)$ . To see the positions of the atoms relative to the cubic axes, the atoms are shown within a cube of 20 Å on a side, from which one corner was cut; this cut corner reveals a (111) face. The lattice translations in the (111) face of silicon (face-centered cubic,  $a = 5.431$  Å) form a two-dimensional lattice. This lattice is shown in Fig. 1 as a fine-line grid. It is shown both at the bottom of the figure to demonstrate the translations and the atoms, and at the top of the figure for clarity. The sides of each of the little rhombes (the "unit cells" of that grid) are  $5.431 \text{ Å} / \sqrt{2} = 3.840 \text{ Å}$ , and they are oriented parallel to the  $[1\bar{1}0]$ ,  $[01\bar{1}]$ , or the  $[\bar{1}01]$  directions. Similarly, the lattice

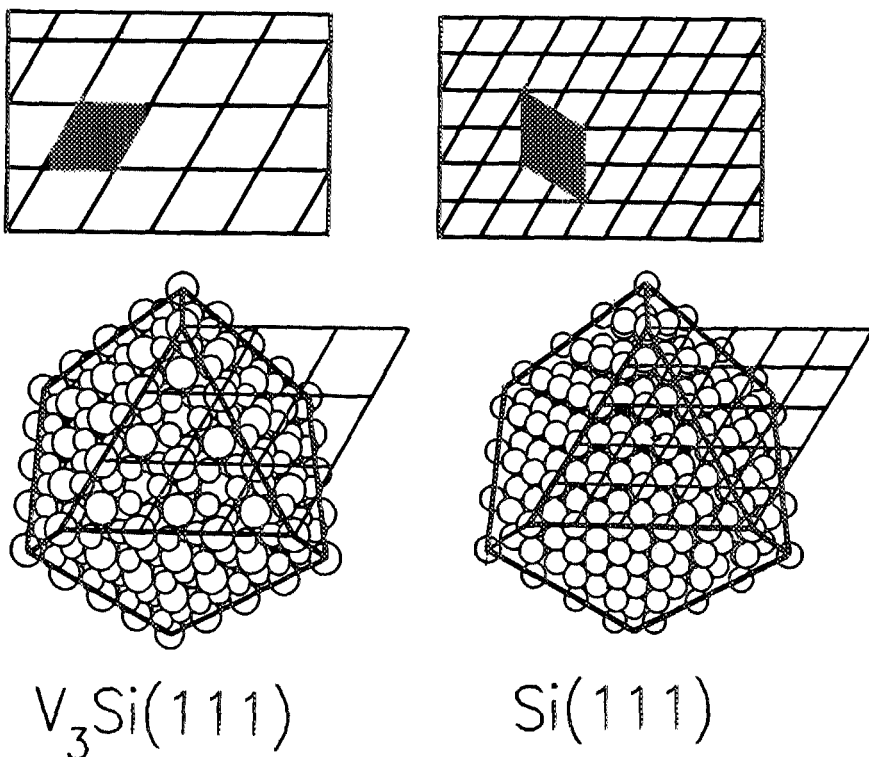


FIG. 1. Lattice match of  $V_3Si(111)$  on  $Si(111)$ . The atomic positions for both materials are shown in the lower part of the figure ( $V_3Si$  on the left, silicon on the right). The atoms are shown as spheres packed in a  $20 \times 20 \times 20$ -Å cube oriented parallel to the cubic axes. One corner of each cube is cut in a (111) plane, and the viewer is looking down the (111) direction. The translational symmetry parallel to the (111) face is shown as a grid of 60° rhombes. Larger unit cells can be formed on those grids to obtain a good match; in this case a larger unit cell containing three silicon unit cells, as shown in the upper right corner, matches almost precisely (0.4%) the  $V_3Si$  original unit cell.

translations perpendicular to the (111) face of  $V_3Si$  (simple cubic,  $\beta$ - $W$  structure,  $a = 4.722 \text{ \AA}$ ) form a similar rhombic grid whose unit cell dimensions are  $4.722 \text{ \AA} \times \sqrt{2} = 6.678 \text{ \AA}$ . One can, therefore, form a superlattice on the silicon surface, whose unit cell is composed of three silicon unit cells as shown in Fig. 1. This larger unit cell is oriented such that its sides are parallel to the  $[1\bar{2}1]$ ,  $[11\bar{2}]$ , or  $[211]$  directions, and their lengths are  $5.431 \sqrt{3/2} = 6.652 \text{ \AA}$ , or less than 0.4% off the  $V_3Si$  unit cell. These two unit cells are shaded in the upper part of Fig. 1.

One can see that the lattice match, as defined here, is characterized by two parameters: the mismatch and the common-unit-cell dimensions. In the example given in Fig. 1, the mismatch is 0.4% and the common unit-cell area is approximately  $38 \text{ \AA}^2$  (38.32 for the silicon, 38.62 for the  $V_3Si$ ). In the most general case, the common unit cell is not necessarily a rhombus, like in Fig. 1, but rather a parallelogram, whose sides are  $a$  and  $b$ , with an acute angle  $\alpha$  between them. These three parameters, namely,  $a_1$ ,  $b_1$  and  $\alpha_1$  for the substrate, may be slightly different for the corresponding  $a_2$ ,  $b_2$ , and  $\alpha_2$  of the film. This difference determines the *mismatch* ( $\epsilon$ ) of the match:

$$\epsilon = \max \left( \left| \frac{a_1 - a_2}{a_1} \right|, \left| \frac{b_1 - b_2}{b_1} \right|, \left| \frac{\alpha_1 - \alpha_2}{\alpha_1} \right| \right).$$

The area of the common parallelogram, i.e.,

$$A = ab \sin \alpha$$

is the other parameter relevant to lattice match (there are actually two areas,  $A_1$  and  $A_2$ , corresponding to the substrate and the film, but they are very close to each other). For every

choice of maximal area and mismatch, the number of possible matches is finite, and all of them can be found in a way that was described in our previous paper.<sup>10</sup> We would like to emphasize that the procedure described above does not ensure that the silicon atoms in the substrate are aligned with the silicon atoms in the silicide. It does ensure, however, that any alignment of the silicide atoms with respect to the silicon atoms can repeat itself periodically along the interface.

A sample of our results is given in Table I. In this table we list only the few best matches, i.e., those with mismatch of 0.5% or less in all three parameters  $a$ ,  $b$ , and  $\alpha$  of the common unit cell, and unit-cell area of  $50 \text{ \AA}^2$  or less. Under these conditions, we have scanned every known transition-metal silicide and tried to match it to the (100), (110), or (111) faces of silicon. Since the restrictions on the match were very tight (0.5% mismatch and  $50\text{-}\text{\AA}^2$  cell area), only five silicides were found to match. These are the  $V_3Si$  [simple cubic,  $a = 4.722$  (Ref. 12)],  $Ni_3Si_2$  [trigonal,  $a = 5.617$ ,  $\alpha = 72^\circ 50'$  (Ref. 13)],  $NiSi_2$  [face-centered cubic,  $a = 5.407$  (Ref. 14)],  $\gamma\text{-}Y_3Si_5$  [hexagonal,  $a = 3.842$ ,  $c = 4.144$  (Ref. 15)], and  $RuSi$  [simple cubic,  $a = 4.703$  (Ref. 16)].

Much more extensive tables, similarly structured but with less tight matches (up to 3% mismatch and  $150\text{-}\text{\AA}^2$  unit-cell area) are deposited at the Physics Auxiliary Publication Service (PAPS),<sup>17</sup> and can be requested from the editor of this journal. Matches of up to 2% mismatch and  $80\text{-}\text{\AA}^2$  unit-cell area are shown graphically in Fig. 2. These matches are shown on the mismatch versus unit-cell area plane, and they cluster (as expected) near the upper right corner, corresponding to poor match (both large mismatch and large unit-cell area). For every pair of matching faces only one point

TABLE I. The best lattice matches of transition-metal silicides on silicon. The primitive common unit cells in this table do not exceed  $50 \text{ \AA}^2$ , and the mismatch is less than 0.5%. Under these conditions, all the possible matches of the silicides on Si (100), (110), and (111) are given in this table. For each possible match, we give here the epitaxial condition, as well as the common unit cell dimensions on each side of the interface. The epitaxial condition is a pair of crystal directions, one on each side of the interface, that will be parallel to each other. Many such pairs are possible, and only one of them is given here. The cells' dimensions in angstroms and degrees are given here for comparison. The mismatch percentage in all the three dimensions of the common unit cell is given in the last three columns.

Matching faces	Epitaxial condition	Cell area ( $\text{\AA}^2$ )	Silicide			Silicon			% <sub>a</sub>	% <sub>b</sub>	% <sub><math>\alpha</math></sub>
			a	b	$\alpha$	a	b	$\alpha$			
$V_3Si(111)/Si(111)$	$[10\bar{1}]  [1\bar{2}1]$	39.	6.68	6.68	60.00	6.65	6.65	60.00	0.4	0.4	0.0
$Ni_3Si_2(111)/Si(111)$	$[1\bar{1}0]  [1\bar{2}1]$	39.	6.67	6.67	60.00	6.65	6.65	60.00	0.3	0.3	0.0
$NiSi_2(111)/Si(111)$	$[1\bar{1}0]  [1\bar{1}0]$	13.	3.82	3.82	60.00	3.84	3.84	60.00	0.4	0.4	0.0
$NiSi_2(511)/Si(111)$	$[01\bar{1}]  [01\bar{1}]$	38.	3.82	10.12	79.11	3.84	10.16	79.11	0.4	0.4	0.0
$NiSi_2(100)/Si(100)$	$[011]  [011]$	15.	3.82	3.82	90.00	3.84	3.84	90.00	0.4	0.4	0.0
$NiSi_2(221)/Si(100)$	$[1\bar{1}0]  [01\bar{1}]$	44.	3.82	11.47	90.00	3.84	11.52	90.00	0.4	0.4	0.0
$NiSi_2(110)/Si(110)$	$[1\bar{1}0]  [1\bar{1}0]$	21.	3.82	5.41	90.00	3.84	5.43	90.00	0.4	0.4	0.0
$Y_3Si_5(0001)/Si(111)$	$[2\bar{1}\bar{1}0]  [1\bar{1}0]$	13.	3.84	3.84	60.00	3.84	3.84	60.00	0.1	0.1	0.0
$RuSi(111)/Si(111)$	$[10\bar{1}]  [1\bar{2}1]$	38.	6.65	6.65	60.00	6.65	6.65	60.00	0.0	0.0	0.0

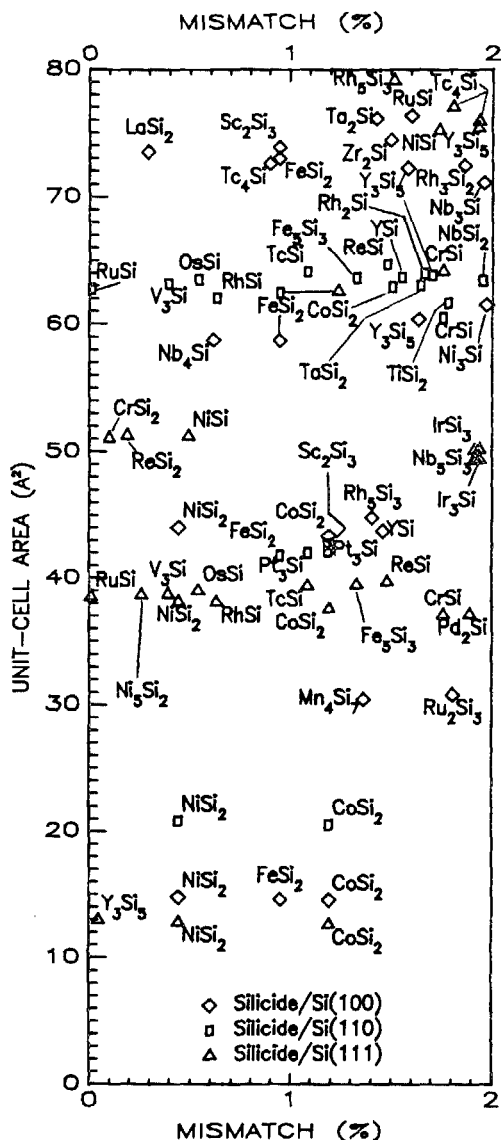


FIG. 2. Lattice matches of transition-metal silicides on silicon (100), (110), (111). All the possible matches such that the mismatch is smaller than 2%, and the common unit-cell area is smaller than  $80 \text{ \AA}^2$  are considered. These matches are characterized by mismatch and unit-cell area, and are shown here as diamonds for matches on silicon (100), rectangles for matches on silicon (110), and triangles for matches on silicon (111). Only the better matches are labeled. All the matches as well as the relative orientations can be found in a set of tables deposited at the PAPS.<sup>17</sup>

(corresponding to the smallest cell area) is shown in Fig. 2, for lack of space in that figure. Different faces of either the silicide or the silicon, however, are shown separately on Fig. 2. For example, the five  $\text{NiSi}_2$  points in Fig. 2, all at 0.44%, correspond to  $\text{NiSi}_2(111)/\text{Si}(111)$ ,  $\text{NiSi}_2(100)/\text{Si}(100)$ ,  $\text{NiSi}_2(110)/\text{Si}(110)$ ,  $\text{NiSi}_2(511)/\text{Si}(111)$ , and  $\text{NiSi}_2(221)/\text{Si}(100)$ , respectively, from the bottom of Fig. 2. The three faces of the substrate considered, namely, (100), (110), and (111) are shown in Fig. 2 as diamonds, rectangles, and triangles. The corresponding faces of the silicides are not shown in Fig. 2, and the reader is referred to our tables<sup>17</sup> for that information. The best matches at the lower left corner of Fig. 2 are the same matches appearing in Table I.

It is interesting to compare the experimentally known cases of epitaxial growth with the lattice-match predictions

presented here. Seven transition-metal silicides are currently known to grow epitaxially on silicon. These are  $\text{NiSi}_2$ ,<sup>18-28</sup>  $\text{CoSi}_2$ ,<sup>9,23,27,29-32</sup>  $\text{Pd}_2\text{Si}$ ,<sup>19,21,23,25,33-46</sup>  $\text{PtSi}$ ,<sup>21,24,47-54</sup>  $\text{Pt}_2\text{Si}$ ,<sup>52,53</sup>  $\text{FeSi}_2$ ,<sup>55</sup> and  $\text{CrSi}_2$ .<sup>56</sup> Out of these seven, the three that correspond to good lattice match, namely,  $\text{NiSi}_2$  (0.4% mismatch),  $\text{CoSi}_2$  (1.2%), and  $\text{Pd}_2\text{Si}$  (1.8%–2.3%), grow as single crystals.<sup>57</sup> The other two,  $\text{PtSi}$  and  $\text{Pt}_2\text{Si}$ , also grow epitaxially (in the sense that the crystallites in the film have preferred orientations with respect to the substrate) despite a large mismatch, but the resulting  $\text{PtSi}$  and  $\text{Pt}_2\text{Si}$  films are polycrystalline.<sup>53</sup> The mismatch between the  $\text{Pt}_2\text{Si}[100]$  and  $\text{Si}[110]$  is 2.4%, and that between  $\text{PtSi}[001]$  and  $\text{Si}[110]$  is 3.0%. Ben Ghoulene *et al.*<sup>53</sup> list several other preferred orientations of the platinum silicides with respect to the silicon substrate; the mismatch in all of them is at least 3%. No information is yet available for the crystalline quality of epitaxial  $\text{FeSi}_2$  and  $\text{CrSi}_2$ , but they would correspond to good lattice match (0.1% for  $\text{CrSi}_2$ , 1.0% for  $\text{FeSi}_2$ , see Fig. 2). On the other hand, epitaxial  $\gamma\text{-Y}_3\text{Si}_5$  or  $\text{RuSi}$ , for example, have not been reported, despite a very good lattice match. In view of these experimental results, one can conclude that lattice-match considerations alone are insufficient to determine all silicide films that grow epitaxially. A correlation between lattice match and epitaxy does seem to exist, though. Some other systems, however, most notably silicon (100) on sapphire (1102), demonstrate that good lattice match is not always necessary for a single-crystalline film<sup>58</sup>; the mismatch in this case is 12.5%. One can see, therefore, that no definitive statements regarding heteroepitaxy can be made based on the criterion of lattice match alone.<sup>58</sup> The reason is that this criterion takes into account only the geometry of the substrate and the film, but not the chemistry between them. Hence, only a combination of chemical and geometrical considerations may yield accurate predictions regarding heteroepitaxial growth. Despite this fact, a comprehensive listing of good matches is useful to designate some silicide films as better candidates than others for epitaxial growth. Moreover, the lattice-match criterion is straightforward to apply, and one can scan all the possible phases of transition-metal silicides (well over one hundred such phases) and compare systematically all the possible crystal faces and relative orientations, as was done in this work.

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